additional bands were observed in this region at −185° or by varying the Ca(OH)A particle size from 200 to 2 μ or by varying pellet formation pressures from 10 to 50 tons/in.^{2}.

Although $\nu_3 - \nu_4$ difference bands are allowed in the 520-400-cm^{-1} region, it is questionable whether the weak Ca(OH)A band at about 425 cm^{-1} reported by Bhatnagar[14,38] is characteristic of powdered samples of pure crystalline stoichiometric Ca(OH)A. However, a definite band is observed at about 435 cm^{-1} in the spectra of Ca(OH)A ignited under certain conditions. This band at about 435 cm^{-1} (not attributed to second phases of $Ca_3(PO_4)_2$ or $Ca_4(PO_4)_2O$) in the spectrum of partially dehydroxylated Ca(OH)A effected by thermal treatment may arise from vibrational motion of $Ca^{2+}{}_3$-O^{2-} groups along the column where the O^{2-} ion has replaced the OH^- ion.[25] Identification and assignment of this band utilizing isotopic calcium and oxygen will be given elsewhere.

Registry No. CFA, 1306-05-4; Ca(OH)A, 1306-06-5; Sr(OH)A, 12266-00-1; Ba(OH)A, 12356-34-2; D_2, 7782-39-0; ^{18}O, 14797-71-8; ^{44}Ca, 14255-03-9; ^{48}Ca, 13981-76-5; $Ca_5F(PO_4)_3$, 12015-73-5; $Ca_5(OH)(PO_4)_3$, 12167-74-7; $Sr_5(OH)(PO_4)_3$, 12195-53-8; $Ba_5(OH)(PO_4)_3$, 12377-63-8.

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Infrared Studies of Apatites. II.
Preparation of Normal and Isotopically Substituted Calcium, Strontium, and Barium Hydroxyapatites and Spectra–Structure–Composition Correlations

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Procedures are described for preparation of calcium, strontium, and barium hydroxyapatites, their deuterated analogs, and calcium hydroxyapatite enriched with isotopic calcium with particular emphasis on purity, stoichiometry, crystal perfection, and gravimetrically monitoring the apatite composition. The effects of low temperature and differences in physical properties of the apatites on the infrared vibrational frequencies are discussed. Shifts in the internal phosphate modes to higher frequencies, in the barium–strontium–calcium hydroxyapatite sequence and also on cooling, are attributed primarily to increased interphosphate repulsion concomitant with lattice contraction. Causes for variation in the frequencies and intensities of the OH modes are considered from several viewpoints including the presence of weak OH- - -O bonding which is neither conclusively established nor rejected. Marked increases in OH band intensities in the barium–strontium–calcium hydroxyapatite sequence are attributed to differences in OH bonding rather than to other effects.

Introduction

Pure stoichiometric hydroxyapatites, $M_{10}(PO_4)_6(OH)_2$ (M = Ca, Sr, Ba), are difficult to prepare from solution. The precipitated calcium hydroxyapatite is usually nonstoichiometric with a Ca:P ratio less than theoretical and contains acid phosphate, carbonate, and excess water.[1] Precipitated nonstoichiometric calcium hydroxyapatites thermally annealed (*e.g.*, 900° in air) to reduce volatile impurities and increase crystallinity yield second phases of β-$Ca_3(PO_4)_2$ and CaO for Ca:P ratios less than and greater than 1.67, respectively.[2] The apatite nonstoichiometry and second phases can be minimized by direct thermal combination of the appropriate reactants in the solid state. The stoichiometry and purity of the solid-state apatite preparations are limited, primarily, only by the purity and stoichiometry of the reactants, provided sufficient time is allowed for thermal diffusion for reaction completion and there is no volatilization of essential components during ignition.

Hydrothermal bomb methods, employing restricted chemical compositions,[3] yield essentially single phases of well-crystallized calcium hydroxyapatite; however, specialized apparatus is required and quantities produced are usually small.

Procedures are described in this paper for solid-state preparation of calcium hydroxyapatite, Ca(OH)A, strontium hydroxyapatite, Sr(OH)A, barium hydroxyapatite, Ba(OH)A, mixed calcium–strontium hydroxyapatite, their deuterated analogs, and precipitated Ca(OH)A enriched with isotopic calcium, with particular emphasis on purity, stoichiometry, crystal perfection, and gravimetrically monitoring the apatite composition.

These apatite preparations were utilized in the preceding paper[4] for infrared vibrational assignments. The effects of low temperature and differences in physical properties of the apatites on the infrared frequencies and causes for hydroxyl frequency and intensity differences are considered in this paper.

Experimental Section

Apatite Preparations. 1. Calcium, Strontium, and Barium Hydroxyapatites. These apatites were prepared in the solid state according to the reactions[5]

$$2MHPO_4 \xrightarrow[\text{air}]{1000^\circ} M_2P_2O_7 + \overline{H_2O} \qquad (1)$$

$$3M_2P_2O_7 + 4MCO_3 \xrightarrow[\text{vacuum}]{1100^\circ} 10MO\cdot 3P_2O_5 + \overline{4CO_2} \qquad (2)$$

$$10MO\cdot 3P_2O_5 \xrightarrow[H_2O,\ 1.5\ \text{atm}]{900\text{–}1100^\circ} M_{10}(PO_4)_6(OH)_2 \qquad (3)$$

The reactions were carried out in a controlled atmosphere in a tube inserted in a furnace. This apparatus consisted of a no. 310 stainless steel tube 18 in. long, with a 1$^5/_8$-in. inside diameter and $^1/_8$-in. wall, closed on one end and threaded on the other to fit a brass cap. The cap was fitted with a Teflon gasket for sealing and had

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[1] See W. E. Brown, *Clin. Orthop. Related Res.*, 44, 205 (1966), and W. E. Brown in "International Symposium on Structural Properties of Hydroxyapatite and Related Compounds, Gaithersburg, Md., Sept 12-14, 1968," Gordon and Breach, New York, N. Y., in press, for summary of causes of nonstoichiometry.

[2] O. R. Trautz, *Ann. N. Y. Acad. Sci.*, 60, 696 (1955).

[3] H. C. W. Skinner, *Amer. J. Sci.*, in press.

[4] B. O. Fowler, *Inorg. Chem.*, 13, 194 (1974).

[5] In reactions 2 and 3, $10MO\cdot 3P_2O_5$ represents the gross chemical composition of the intermediate solid phase.

three ports: one each for steam entry and exit or vacuum and a third for a sliding thermocouple enclosed in a Vycor glass tube. The closed-end section of the tube was placed in an electric furnace, and the space around the tube on the open end of the furnace was closed with a fitted fire brick. A $1^{1}/_{2}$-in. diameter Vycor tube sealed on one end was used for a liner in the ignition tube to avoid sample contamination from the metal tube. The samples, contained in platinum crucibles, were inserted into the tube by means of a Vycor tray. Water vapor at 1.5 atm, passed through the tube at a rate of approximately 10 l./min, was generated by a commercial pressure cooker placed on hot plates. Distilled water, at about 30 psi, was introduced into the pressure cooker by means of a float-controlled valve which maintained a constant water supply for continuous water vapor generation.

The $MHPO_4$ salts were ignited at 1000° in air for 12 hr to ensure total dehydration and conversion to the pyrophosphate which served as a better and more stable weighing form than $MHPO_4$. A 3–4 M mixture of the $M_2P_2O_7$ and MCO_3 salts was mixed and ground to less than 10 μ in particle size in an acetone slurry contained in a capsule with balls, both made of hardened stainless steel, mounted on a mechanical shaker. The reaction mixtures, pressed into pellets in a die to ensure a better solid-state reaction, were dried at 200° to constant weight in tared platinum crucibles and then ignited at 1100–1175° under vacuum for CO_2 removal which was quantitatively ascertained from the sample weight loss. The samples ignited under vacuum either were brought to atmospheric pressure in dry nitrogen before cooling and weighing or, preferably, were cooled to room temperature under vacuum to avoid reaction with atmospheric H_2O vapor which proceeds rapidly at the higher temperatures. The resultant essentially CO_2-free mixtures, maintained at 900 to 1100°, were treated with H_2O vapor at 1.5 atm and the H_2O uptake was established by the sample weight increase.

The $CaHPO_4$ and MCO_3 salts were reagent grade chemicals; the $SrHPO_4$ was prepared according to one of the procedures given by Mooney, *et al.*[6] ($(NH_4)_2HPO_4$ solution added to $Sr(NO_3)_2$ solution at 5°), and the $BaHPO_4$ was prepared according to the procedure given by Lehr, *et al.*[7]

The phosphorus contents of the apatites were determined by the method of Gee and Deitz.[8] *Anal.* Calcd for $Ca_{10}(PO_4)_6(OH)_2$: P, 18.49. Found: P, 18.50. Calcd for $Sr_{10}(PO_4)_6(OH)_2$: P, 12.56. Found: P, 12.49. Calcd for $Ba_{10}(PO_4)_6(OH)_2$: P, 9.40. Found: P, 9.39. The X-ray diffraction patterns indicated single phases of well-crystallized apatites.

These solid-state reactions for preparing the apatites are similar to those used by Klement[9] and Klement and Dihn[10] for preparing Sr- and Ba(OH)A, respectively; however, a different sequence of reactions and different conditions and reactants were used for the preparations described here.

2. **Deuterated Apatites.** The deuterated analogs were prepared by treating the apatites formed by reaction 3 with excess D_2O vapor at high temperature. The apatite samples, wrapped in platinum foil, and D_2O were sealed inside nitrogen-flushed Vycor glass tubes (5-mm inside diameter, 1-mm wall) and then ignited. The Ca- and Sr(OH)A samples were deuterated at 20–30 atm D_2O pressure at 900° for 12 hr and the Ba(OH)A sample was deuterated at about 5 atm at 600° for 140 hr. Duplicate conditions using H_2O were carried out. Infrared spectra of the Ca- and Sr(OH)A treated in 20–30 atm H_2O pressure at 900° for 12 hr were essentially identical with spectra of the apatites prepared in 1.5 atm H_2O pressure at 900° for 24 hr. The Ba(OH)A was deuterated at the lower temperature and pressure because the Ba(OH)A decomposed at 900° (24 hr) in 5 atm H_2O pressure. The H_2O and D_2O partial pressures for all sealed-tube runs were calculated assuming ideal gas behavior and are, therefore, approximate values. All sealed-tube runs contained high-purity nitrogen as the second gas phase.

3. **Isotopically Enriched Calcium Hydroxyapatites.** The Ca(OH)A enriched with ^{18}O was prepared by heating $10CaO{\cdot}3P_2O_5$ compositions with excess $H_2{}^{18}O$ vapor in sealed platinum tubes at 900°; preparation and ^{18}O–^{16}O exchange details will be given elsewhere.

The Ca(OH)A enriched with isotopic Ca was prepared by precipitation utilizing $CaCO_3$ containing 94 and 78% ^{44}Ca and ^{48}Ca, respectively. A $^{40}Ca(OH)A$ sample was prepared by the same procedure. A 6-mg sample of $CaCO_3$ in 0.3 ml of H_2O contained in a conical-bottom centrifuge tube was neutralized with 0.02 ml of 8 M HNO_3 and then basified with 0.3 ml of concentrated NH_4OH. A stoichiometric quantity of $NH_4H_2PO_4$ in 0.3 ml of 5 M NH_4OH was added dropwise by means of a capillary to the basic Ca solution yielding a final volume, including 1.5 ml of 5 M NH_4OH washings, of 2.4 ml at pH of about 11. The centrifuge tube containing the reaction mixture, firmly sealed with a rubber stopper fixed to the tube with wire, was heated at 65° for 3 days. The precipitate (not washed after centrifugation) was ignited by slowly raising the temperature from 25 to 900° over a period of 3 hr and then continuing at 900° in water vapor at 1.2 atm for 40 hr to remove volatile impurities and to perfect the apatite.

4. **Mixed Calcium–Strontium Hydroxyapatites.** These mixed-cation apatites were prepared in the solid state by igniting intimately mixed and pressed samples containing the appropriate amounts of the MO, $M_2P_2O_7$, or MPO_3 salts (overall $10MO{\cdot}3P_2O_5$ composition) in 1.5 atm H_2O pressure at 900–1100° for 24 hr. Only an apatite with lattice dimensions intermediate between those of the end members was detected by X-ray diffraction. Both the X-ray diffraction data and the intermediate infrared frequencies observed for these apatites are in agreement with the isomorphic Ca–Sr substitution as reported by Collin.[11]

Infrared Absorption Measurements. Infrared spectra of the apatites in the 4000–200-cm^{-1} region at 48 and −185° and vibrational assignments are given in the preceding paper.[4]

Results and Discussion

Apatite Preparations. The gravimetric data for the solid-state apatite preparations are given in Table I. The residual CO_3 contents of the $10CaO{\cdot}3P_2O_5$ and $10SrO{\cdot}3P_2O_5$ samples ignited at 1100° under vacuum were estimated from the gravimetric data to be about 0.04 and 0.07%, respectively. The chemical group arising from the weight increase of the anhydrous $10MO{\cdot}3P_2O_5$ samples ignited in H_2O vapor was qualitatively identified as the OH ion from the infrared spectra, and the sample weight increase was used as a quantitative index to establish the OH contents of the apatites. The $10CaO{\cdot}3P_2O_5$ and $10SrO{\cdot}3P_2O_5$ samples treated in 1.5 atm H_2O pressure at 900° showed 99 and 94%, respectively, of the theoretical H_2O gain. Further treatment of the $10SrO{\cdot}3P_2O_5$ sample in H_2O vapor at 1100° did not yield additional weight increase.

The high thermal stabilities of $BaCO_3$ (dissociation pressure 1 atm at about 1432°[12]), BaO_2 (dissociation pressure 1 atm at 840°; mp 450°), and $Ba(OH)_2$, which melts at 325° and reaches a dissociation pressure of 1 atm at about 998°[13] or at about 1090°,[14] introduce possible competitive reactions and melt separations in the solid-state preparation of Ba(OH)A dependent upon the experimental conditions employed and the relative stability of Ba(OH)A. In the initial hydration of the $10BaO{\cdot}3P_2O_5$ phase at 1100°, the H_2O pressure (1.0–1.5 atm) was below that necessary (2.4 atm[13]) or slightly above (1.1 atm[14]) to form the hydroxide, and the CO_2 partial pressure arising from the preboiled water source was below that necessary to form $BaCO_3$ (10.6 mm at 1100°[12]). Additional treatments of the original Ba(OH)A and the product of reaction 2 were carried out both above and below the pressures necessary to form the peroxide, carbonate, and hydroxides of barium.

The $3Ba_2P_2O_7 + 4BaCO_3$ reaction mixture ignited under vacuum ($<10^{-4}$ atm) at 1100° for 16 hr and continued at 1175° for 19 hr had residual CO_2 contents of 0.5 and 0.3%, respectively, as determined by the weight loss data. Higher

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Table I. Gravimetric Data for Apatite Reactants Ignited under Vacuum and Water Vapor

	Conditions[a]			Wt % CO_2 loss		Wt % H_2O gain[b]		
Reactants	Temp, °C	Atm	Time, hr	Calcd	Obsd[c]	Calcd	Obsd[c]	Obsd/calcd
$3Ca_2P_2O_7 + 4CaCO_3$	1100	Vac	20	15.14	15.11 ± 0.00			
	900	H_2O	24			1.826	1.801 ± 0.003	0.986 ± 0.002
$3Sr_2P_2O_7 + 4SrCO_3$	1100	Vac	16	10.75	10.70 ± 0.00			
	900	H_2O	21			1.232	1.157 ± 0.002	0.939 ± 0.002
	1100	H_2O	6				1.157 ± 0.003	0.939 ± 0.003
$3Ba_2P_2O_7 + 4BaCO_3$	1100	Vac	16	8.24	7.79 ± 0.00			
	1175	Vac	19		7.93 ± 0.00			
	1100	H_2O	21			0.919	0.789 ± 0.005	0.858 ± 0.006

[a] Vac (vacuum) atmosphere, 10^{-4} atm; H_2O atmosphere, 1.5 atm H_2O vapor. [b] $(H_2O)(100)/(3M_2P_2O_7 + 4MO)$. [c] Averages of duplicate or triplicate determinations and average deviations.

temperature could not be attained with the apparatus used. The residual CO_3 was also evident from the infrared spectra which had weak absorption bands at about 1400 and 860 cm^{-1} corresponding to the ν_3 and ν_2 CO_3 vibrational modes, respectively. The $10BaO{\cdot}3P_2O_5$ sample treated in 1.5 atm H_2O pressure at 1100° for 21 hr had a weight increase corresponding to 86% of the theoretical H_2O content, but the sample still contained a few tenths of 1 wt % CO_3. Spectra of a portion of the Ba(OH)A sample further treated at 900° in 1.5 atm H_2O pressure for three 6-hr intervals (sample was ground between intervals) indicated less than 0.3% CO_3. This material was additionally ignited in air and in 5 and 25 atm H_2O pressure in sealed Vycor glass tubes at 300° (240 hr), 600° (140 hr), and 900° (24 hr). The Ba(OH)A treated at 900° (24 hr) in 5 and 25 atm H_2O pressure was not stable as indicated by bands from a second phase, $Ba_3(PO_4)_2$, in the spectra.

The observed lower than theoretical weight increases for complete hydroxylation of the $10SrO{\cdot}3P_2O_5$ and $10BaO{\cdot}3P_2O_5$ samples may, in part, arise from a reduction in the residual CO_3 contents of these samples during hydrothermal treatment. Concomitant loss of the residual CO_2 and gain in H_2O would yield a net weight increase less than the actual H_2O uptake.

The stoichiometry and purity of the solid-state apatite preparations are limited, primarily, only by the purity of the starting materials, $MHPO_4$ and MCO_3, provided sufficient time is allowed for thermal diffusion for reaction completion and there is no volatilization of essential components during ignition. The gravimetric data detected no volatilization from the $10MO{\cdot}3P_2O_5$ mixtures under the experimental conditions used. Nonconstitutional H_2O and CO_3 impurities can be essentially eliminated and the OH content can be quantitatively inferred by the gravimetric analysis.

Infrared studies of the stoichiometric apatites with varying degrees of hydroxylation established gravimetrically by reversing reaction 3 in the absence of water will be given elsewhere along with the phases formed by reaction 2 which were (a) apatitic in structure for the 10SrO- and $10BaO{\cdot}3P_2O_5$ compositions (*i.e.*, indicating the oxyapatite $M_{10}(PO_4)_6O$) and (b) mixtures of β-$Ca_3(PO_4)_2$ and $Ca_4(PO_4)_2O$ for the $10CaO{\cdot}3P_2O_5$ composition.

Infrared Spectra. 1. Intermolecular and Temperature Effects on Absorption Frequencies. Plots of frequencies of the corresponding vibrational modes of the Ca-, Sr-, and Ba(OH)A against increasing mass of the cation, ionic radius of the cation, or lattice dimensions of the apatites are almost linear. Plots of the corresponding vibrational frequencies of the apatites *vs.* *a*-axis dimensions, which of course reflect the cation mass and ionic radii (Table II), are shown in Figure 1. Except for the plot of the frequencies of the OH stretching modes, which increase in the sequence Ca-, Sr-, Ba(OH)A,

Table II

	Cation ionic	Unit cell dimensions, Å		
Apatite	radius, Å	*a* axis	*c* axis	Ref
$Ca_{10}(PO_4)_6(OH)_2$	0.99	9.421	6.882	*a*
$Sr_{10}(PO_4)_6(OH)_2$	1.12	9.765	7.280	*b*
$Ba_{10}(PO_4)_6(OH)_2$	1.34	10.177	7.731	*b*

[a] Averaged values from R. Wallaeys, *Ann. Chim.* (*Paris*), 7, 808 (1952); D. Calstrom, *Acta Radiol., Suppl.*, No. 121 (1955); and ref 2. [b] Reference 37.

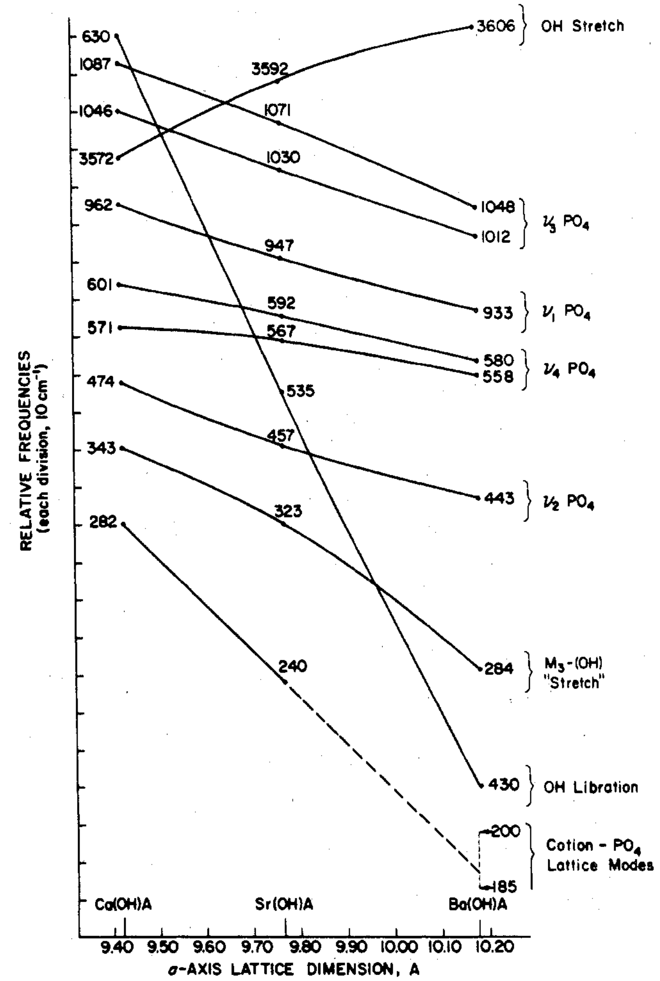

Figure 1. Plots of the infrared frequencies (cm^{-1}) at 48° of the corresponding vibrational modes of calcium, strontium, and barium hydroxyapatites *vs.* the *a*-axis lattice dimensions of the apatites. The frequencies are plotted on a relative ordinate scale where each division equals 10 cm^{-1}. The shoulders in the ν_3 region are not plotted, and the two lower frequency ν_4 components are plotted as average values.[4] The highest frequency Ba-PO_4 lattice mode, occurring below the low-frequency limit of the spectrophotometer, is indicated by extrapolation.

Table III. Effect of Temperature on Infrared Frequency Positions of Vibrational Modes of Calcium, Strontium, and Barium Hydroxyapatites[a]

Internal modes	Absorption region, cm^{-1}	Approx freq shift on cooling,[b] cm^{-1}	Lattice modes	Absorption region, cm^{-1}	Approx freq shift on cooling,[b] cm^{-1}
OH str	3600	+3	OH lib	500	−3
PO_4, ν_3	1050	+3	M_3-(OH)	300	+3 to +9
ν_1	950	+2	M-PO_4	<300	+5 to +10
ν_4	575	0 to +1			
ν_2	450	+1			

[a] Detailed spectra are given in the preceding paper.[4] [b] Frequencies at −185° minus frequencies at 48°.

plots of all the other frequencies decrease nearly linearly with increasing *a*-axis dimension. The plot of the OH librational modes has the greatest slope, about 5-15 times those of the internal phosphate modes, which clearly illustrates the sensitivity of this vibrational mode to the environment of the OH ion. The slope of the plot of the Ca- and Sr(OH)A bands at 282 and 240 cm^{-1}, assigned to cation-PO_4 lattice modes,[4] is about 3-6 times those of the internal phosphate modes. The greater slope of this line is consistent with the assignment of these bands to external modes because the frequencies of these modes are directly related to cation mass and cation-anion intermolecular forces whereas the frequencies of the internal modes are related primarily to PO intramolecular forces. The corresponding Ba(OH)A lattice mode is indicated, by the extrapolation in Figure 1, to occur at slightly less than 200 cm^{-1}. The internal PO_4 modes, the internal OH stretching mode, and the OH librational modes occur at essentially the same frequencies in ^{40}Ca-, ^{44}Ca-, and ^{48}Ca-(OH)A.[4] The insensitivity of these frequencies to cation mass rule out cation mass as a significant factor contributing to the frequency differences of the internal modes in these apatites.

Differences in the frequencies of the internal vibrational modes of the same anion having the same site symmetry in different compounds have been related to (a) cation mass, (b) cation ionic radius, (c) cation coordination number, (d) cation polarizing power, (e) type of cation-anion bonding, and (g) electronic configuration of the cations. Weir and Lippincott[15] have attributed shifts in internal frequencies of the same anion in isostructural compounds having cations with the same type or similar type of electronic configuration but varying in mass and ionic radius to the effect of cation ionic radius. As the lattice contracts with decreasing cation ionic radius, increases in the internal anion frequencies were attributed to the effect of increased anion-anion repulsion. Irregularities in anion frequency-cation ionic radius trends for the same anion in isostructural lattices having cations from different periodic groups have been, in part, related to differences in cation electronic configuration (*i.e.*, differences in ionic character of the cation-anion bond).[15-17] Increases in the internal frequencies of the same anion in isostructural compounds having cations of the same periodic groups also correlate with increases in cation polarizing power;[18] however, both cation ionic radius and anion-anion separation decrease as the cation polarizing power increases.

At −185° the corresponding absorption bands of Ca-, Sr-, and Ba(OH)A show systematic shifts (Table III) and intensity changes.[4] As an effect of cooling, all the vibrational frequencies, except the OH librational frequencies and one ν_4 PO_4 frequency, shift to higher frequencies.

Baddiel and Berry[19] reported little or no change in the Ca(OH)A frequencies in the 4000-400-cm^{-1} region on cooling to −185°, except for a decrease in the OH librational frequency which agrees with this study and a decrease in the ν_4 PO_4 frequencies which was not observed in the present study. The frequency shifts on cooling reported in this study are small but were measurable and reproducible.

Schroeder, Weir, and Lippincott[20] pointed out that shifts to higher frequencies are expected for vibrational modes which experience increased repulsive forces effected by decreased intermolecular distances concomitant with lattice contraction on cooling and accordingly that frequencies more directly related to intermolecular forces and distances (lattice modes) should be more temperature dependent than frequencies of the internal modes.

The ν_3 and ν_1 phosphate stretching frequencies shift more than the ν_4 bending modes on cooling which may be caused by decreased anion-anion distances and increased interoxygen repulsion which accordingly could oppose the stretching modes (expansional type modes) more than the bending modes. However, if the lattice contracts anisotropically on cooling, the relative frequency shifts for different modes may vary because of different effects on the spatially oriented transition moments of the vibrational modes. The frequencies assigned to the cation-PO_4 lattice modes shift more on cooling than the frequencies of the internal modes which is expected and is consistent with the assignments. The frequency shifts occurring for the OH modes on cooling will be considered in the next section. The magnitudes and directions of the frequency shifts, except those of the OH modes, observed on cooling are qualitatively consistent with the assumed lattice contraction on cooling to −185°. The frequencies observed at −185° for the internal PO_4 modes and the cation-PO_4 lattice modes plotted on the lines in Figure 1 correspond to a lattice contraction ranging from about 0.02 to 0.06 Å or an average of 0.04 Å or about 0.4% contraction in the *a* axis on cooling to −185°.

The approximately linear increase in frequencies of the internal phosphate modes for these structural analogs as a function of decreasing lattice dimension effected by both decreasing cation ionic radius and cooling and the insensitivity of these frequencies to isotopic mass change (*i.e.*, ^{44}Ca and ^{48}Ca substitution) indicate that the predominant factor causing shifts in the internal PO_4 frequencies to higher energies is increased anion-anion repulsion concomitant with decreased anion-anion separation.

Stutman, *et al.*,[21] have attributed the progressive frequency increase observed for the ν_1 PO_4 mode in the calcium chlor-, calcium hydroxy-, and calcium fluorapatite sequence to in-

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creased localized repulsion of the phosphate oxygens by the increasing proximity of the Cl, OH, and F ions to the plane of the PO_4 ions without regard to the effects of lattice contraction. Figure 1 illustrates the significant frequency dependency of the PO_4 vibrations on the total repulsive forces acting on the entire PO_4 group effected by closer anion-anion packing. In fact, considering lattice contraction only, the internal PO_4 frequencies of calcium fluorapatite plot close to the extrapolated lines in Figure 1. However, in frequency-structure correlations among OH, F, and Cl apatites, both localized environmental differences caused by different relative positions and size of the anions along the column as well as differences in lattice dimensions in all spatial directions will require consideration because of the spatially oriented transition moments of the vibrational modes.

Klee and Engel[22] have correlated the internal PO_4 frequencies of various apatites ($M_{10}(PO_4)_6X_2$, M = Ca, Sr, Ba, Cd, Pb; X = OH, F, Cl, Br) with various properties of the M and X ions including cation mass and the mass, lattice position, and size of the X ions. Of properties considered, the mass of the cation was indicated to have the greatest influence on the mean frequencies of the internal PO_4 vibrational modes, *e.g.*, decreasing trend in mean vibrational frequencies with increasing mass of the cation. However, as shown in the preceding paper,[4] the internal PO_4 frequencies of ^{40}Ca(OH)A, ^{44}Ca(OH)A, and ^{48}Ca(OH)A are essentially the same and thus insensitive to changes in cation mass. The ν_1 PO_4 frequency of ^{48}Ca(OH)A should, according to the cation mass-frequency correlation, shift to lower frequency by about 2.4 cm^{-1}; however, the frequency of this mode (which can be measured with precision because of the band sharpness) differed by no more than ±0.2 cm^{-1} in ^{40}Ca-, ^{44}Ca-, and ^{48}Ca(OH)A; similarily, the sharp bands at 601 cm^{-1} differed by no more than ±0.2 cm^{-1}. A slight splitting and an apparent shift were observed in the ν_4 components at about 571 cm^{-1} of isotopic ^{44}Ca- and ^{48}Ca(OH)A as compared to the corresponding ^{40}Ca(OH)A band; however, the ^{44}Ca- and ^{48}Ca(OH)A band positions are essentially identical. Cation mass differences may have a slight effect on the internal frequencies of the PO_4 ions, but because of the small isotopic cation mass difference between ^{40}Ca and ^{48}Ca, and the broadness of some bands, very minor frequency shifts, a few tenths of 1 cm^{-1} for sharp bands and more for the broad bands, could escape detection; however, frequency shifts of about 1-3 cm^{-1} predicted according to the cation mass-internal frequency correlation were not observed. Tarte and Preudhomme[23] observed no cation mass effect on the internal anion vibrational frequencies of $^{40}CaSiO_3$ and $^{44}CaSiO_3$ whereas with increasing cation ionic radius in the isostructural Sr- and $BaSiO_3$ analogs, nearly all the internal anion frequencies shifted progressively to lower frequencies. Klee and Engel[22] suggested that the greater band splitting and deviation of the internal PO_4 frequencies of the Cd and Pb apatites from the nearly linear cation mass-frequency trends observed for the apatites of Ca, Sr, and Ba arise from more covalent cation-anion bond character in the cadmium and lead apatites as compared to the calcium, strontium, and barium apatites. As the cation-anion bond becomes stronger, the frequencies of the internal modes of the anion should become more cation dependent and in turn more sensitive to cation mass. This may contribute to the lower internal PO_4 frequencies of the cadmium and lead apatites when plotted along with the corresponding calcium, strontium, and barium apatite frequencies all *vs.* cation ionic radius (*i.e.*, approximate lattice dimensions). Spectra of cadmium apatite enriched with isotopic Cd should establish the degree of cation-anion interaction; if the cation-anion bonding is appreciable, slight spectral broadening may occur in apatites containing natural Cd due to the relative abundance of its isotopes.

Spectra of apatites prepared with mixed-cation composition, Ca_7Sr_3- and $Ca_3Sr_7(PO_4)_6(OH)_2$, had vibrational frequencies intermediate between those of Ca(OH)A and Sr(OH)A. The intermediate internal PO_4 frequencies, which shift to lower frequencies as a function of increasing Sr content, are attributed primarily to the effect of decreased anion-anion repulsion concomitant with increased lattice dimensions, and the intermediate frequencies of the modes involving both cation and anion motion, to the effects of increased cation mass and weaker cation-anion bonding. Most of the absorption bands of the mixed calcium-strontium apatites were broadened, especially the hydroxyl bands, as compared to the band widths of the end members, Ca(OH)A and Sr(OH)A. This band broadening reflects the heterogeneity introduced by the different cations in the crystal fields about the vibrating anions. Frequency shifts and band broadening of this type can be expected for apatites containing sufficient substitution of different cations and/or anions which undoubtedly include many biological and natural apatites. A detailed account of the spectral effects of mixed-cation apatites will be given elsewhere.

2. **Hydroxyl Absorption Frequencies.** The OH vibrational modes are of primary interest, especially the OH librational motion which is very sensitive to its environment as evidenced by its frequency differences in these apatites (Figure 1). The Ba-, Sr-, and Ca(OH)A OH stretching modes occur at 3606, 3592, and 3572 cm^{-1}, respectively, and the OH librational modes, at 430, 535, and 630 cm^{-1}, respectively. The decrease in the OH stretching frequency and the marked increase in the librational frequency in the Ba-, Sr-, Ca(OH)A sequence are suggestive of hydrogen-bond trend arising from decreasing OH- - -O separations. Baddiel and Berry[19] suggested weak hydrogen bonding of the OH- - -OPO_3 type may occur in Ca(OH)A because of intermolecular distances and displacements in the hydroxyl frequencies. Blakeslee and Condrate[24] did not observe the continuous increase in the OH stretching frequencies with increasing lattice dimensions shown in Figure 1; *i.e.*, their infrared and Raman OH stretching frequencies for Ca- and Sr(OH)A agree within 1 cm^{-1} of those given here, but they did not detect the Ba(OH)A infrared frequency at 3606 cm^{-1} and reported the Raman shift occurs at 3527 cm^{-1} as compared to the 3607-cm^{-1} shift observed in this study. Also, the OH stretching frequency reported by Balkeslee and Condrate[24] for lead hydroxyapatite at 3573 cm^{-1} (Raman), infrared frequency not reported, is considerably displaced from the OH frequency-lattice dimension trend in Figure 1; this deviation, as already mentioned for the internal PO_4 modes, may be related to the different electronic configuration of lead.

The OH ions in Ca(OH)A, about 3.44 Å apart, are located on and oriented parallel to the sixfold screw axis. The OH ions are displaced about 0.3 Å from, with the proton pointing away from, the nearest trigonal Ca plane.[25] The positions and orientations of the OH ions along the *c* axis have not been determined in Sr- and Ba(OH)A. However, assum-

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ing equivalent OH positions in Sr- and Ba(OH)A and using the *c*-axis lattice dimensions given in Table II give OH to OH distances along the *c* axis of 3.64 and 3.85 Å, respectively. The maximum O–O separation for O–H- - -O bonding has been estimated to be about 3.3 Å,[26] thus minimizing the possibility of OH- - -OH bonding along the *c* axis in these three apatites. The closest oxygen approach to the OH ion is from three oxygens of three phosphate groups which surround the OH ion. This OH oxygen to phosphate oxygen distance[27] in Ca(OH)A is 3.043 Å and the corresponding estimated distances in Sr- and Ba(OH)A are, assuming the same OH positions, 3.14 and 3.28 Å, respectively, all of which are close enough for weak hydrogen bonding. An OH- - -O bond between the OH and OPO_3 ions would be bent because of the OH bond direction along the *c* axis; however, bent OH- - -O bonds are common.[28]

On deuterating Ca(OH)A, the ν_4 PO_4 bending modes change intensity and shift slightly.[4] These band changes could arise from differences in OH- - -OPO_3, OD- - -OPO_3 interactions because the OH- - -O and OD- - -O bond lengths and energies differ,[29] and the different degree of PO_4 perturbation would be reflected in the PO_4 vibrational frequencies and intensities. On deuteration, the corresponding ν_4 bands for Sr- and Ba(OH)A do not display the changes that occur for Ca(OD)A.[4] Because of the greater intermolecular distances in Sr- and Ba(OH)A, differences in vibrational perturbation arising from the possible OH(D)- - -OPO_3 interactions may be too minor to detect. However, as pointed out in the preceding paper[4] the ν_4 band differences observed for Ca(OH)A and Ca(OD)A could arise from slight modifications in the crystal field about the PO_4 ions resulting from different relative positions of the OH and OD ions (with or without H bonding), from a slightly different Ca(OD)A structure, or more probably from interactions with other modes.

At −185° the OH stretching and librational modes have shifted slightly to higher and lower frequencies, respectively (Table III). As a result of lattice contraction on cooling and the expected shortening of O–O distances in OH- - -O bonds, the OH stretching frequency normally shifts to lower frequency and the OH librational frequency shifts to higher frequency. Since just the opposite shifts are observed, this reduces the possibility of appreciable OH- - -OPO_3 interactions in these apatites. However, these opposite band shifts on cooling do not unequivocally exclude the possibility of weak OH- - -OPO_3 interactions.

According to the line slopes in Figure 1, the increases in the OH stretching frequencies and decreases in the OH libration frequencies on cooling correspond to an increase rather than a decrease in specific intermolecular dimensions about the OH ions. This could occur from disproportional lattice changes on cooling resulting in slightly increased OH to OPO_3 distances, but this is unlikely. The M_3–(OH) "stretching" frequencies shift to higher frequencies on cooling, consistent with lattice contraction, but by about twice the amount predicted by shifts in the other vibrational modes.

Similar shifts in frequency with decreasing temperature were observed[30] for the OH stretching and librational modes of $Ca(OH)_2$, a hydroxide in which hydrogen bonding is considered absent because of the large O–O distances, about 3.3 Å.[31] The frequencies of the OH stretching[32] and librational fundamentals,[33] 3644 and about 390 cm^{-1}, respectively, also suggest that OH- - -O interactions, if present, are weak. At −185° the $Ca(OH)_2$ OH stretching mode shifts to higher frequency, 3644 to 3652 cm^{-1}, and the OH librational mode, centered at about 385 cm^{-1}, shifts to 375 cm^{-1}.[30]

Busing and Levy[34] observed, using neutron diffraction, an apparent increase in the OH internuclear distance on cooling $Ca(OH)_2$ from +20 to −140°, but no increase after corrections. The OH ions in $Ca(OH)_2$ are located on C_{3v} sites[34] and have Ca_3–(OH) geometry similar to that in Ca(OH)A: the OH ion sits atop, with the proton pointed away from, a trigonal pyramid formed with the Ca triangle. A very slight increase (about 0.005 Å for the apatites and more for $Ca(OH)_2$) in the OH internuclear distance on cooling and the accompanying increase in the moment of inertia of the OH ion could account for the minor shifts in the OH librational modes to lower frequencies. A closer M_3–(OH) approach on cooling and increased M–H repulsion could tend to increase the OH internuclear distance.

Isotopic frequency shifts and other considerations[4] indicate that the Ca(OH)A mode absorbing at 343 cm^{-1} approximates Ca_3–(OH) stretching which, in turn, implies slight covalent Ca_3–(OH) bonding. As the Ca_3–(OH) bond becomes stronger, the OH librational mode would have less "free OH librational" character and more Ca_3–O–H "bending" character which would contribute to an increase in the frequency of this mode as compared to that of the "unbound" OH group. The high frequency of the OH librational mode in Ca(OH)A is more understandable in terms of slight Ca_3–O–H bending character, especially since the low-temperature data are not in accord with OH- - -O bonding which reduces the possibility that OH- - -O bonding is the major factor contributing to the high frequency of this mode.

3. Hydroxyl Absorption Intensities. The band areas of the hydroxyl modes decrease in the Ca-, Sr-, Ba(OH)A sequence. These relative OH band areas for Ca-, Sr-, and Ba(OH)A are, respectively, approximately as follows: OH stretch, 1:0.5:0.2; OH libration, 1:0.8:0.4; M_3–(OH) "stretch," 1:0.7:0.4. Numerous linear absorbance spectra of equimolar samples of the apatites ground to the same particle size ($\leqslant 5$ μ) and dispersed in pellets ranging in index of refraction (1.46–1.74) demonstrated that the relative OH band area differences, measured directly or normalized to PO_4 band areas, were not spurious.

The OH band intensity differences can be attributed primarily to differences in OH bonding provided that these apatites do not differ significantly in composition, physical properties, and structure.

The magnitudes of the OH band intensity decreases do not appear attributable to a deficiency of OH ions based upon the weight increase concurrent with the hydrothermal treatment or to substitution of other ions for the OH ions.

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During synthesis, the Ca-, Sr-, and Ba(OH)A samples showed weight increases corresponding to 99, 94, and 86%, respectively, of the theoretical OH ion contents. The estimated carbonate content of the samples was highest for Ba(OH)A (about 0.3 wt %). Assuming substitution of CO_3 for two OH ions,[35] this CO_3 content would reduce the Ba(OH)A OH ion content by about 10%. Fluoride and chloride concentrations in the starting reagent grade chemical were apparently low enough to have no detectable effect on the OH band intensities.

The presence of oxyapatite[36] or partial dehydroxylation[37] is very unlikely to account for the lower OH band intensities in these strontium and barium apatites because of their hydrothermal preparation and the accompanying weight increases. In addition, no secondary absorption (possible $M^{2+}{}_3$-O^{2-} "stretching") near the $M^{2+}{}_3$-(OH^-) "stretching" bands was detected. A study of the apatites with varying degrees of hydroxylation established spectroscopically and gravimetrically by reaction 3 (apatite preparations) with emphasis on spectroscopic identification of possible O^{2-} incorporation by means of $M^{2+}{}_3$-O^{2-} "stretching" absorption will be given elsewhere.

The possibility of ions, other than those already mentioned, substituting for the OH ions in Ba(OH)A was considered because of the weak OH band intensities. Peroxide ($O^{2-}{}_2$) substitution for $2OH^-$ in Ba(OH)A was checked because of (a) the absence of infrared absorption for groups other than OH, PO_4, and CO_3, (b) the observed gravimetric data during synthesis which corresponds to the addition of 0.5 mol of O_2 (or 0.9 mol of H_2O) per empirical $Ba_{10}(PO_4)_6O$ formula weight, (c) the high thermal stability of BaO_2 whose dissociation pressure reaches 1 atm at about 840°, and (d) the approximate geometrical fit of the $O^{2-}{}_2$ ion bonded to opposite Ba ions of adjacent Ba triads in the octahedral-type site formed by the six Ba ions in Ba(OH)A which is similar in geometry to the octahedral site of the $O^{2-}{}_2$ ion in BaO_2.[38] The Raman shift assigned to O-O stretching in liquid H_2O_2 occurs at about 880 cm^{-1}.[39,40] Solid BaO_2 has a strong Raman shift at about 840 cm^{-1} which, as expected, was absent in the infrared spectrum. However, no significant absorption was observed in the Raman spectrum of Ba(OH)A in the O-O stretching region, thus minimizing the possibility of the peroxide ion in this apatite.

Slightly lower MO percentages than theoretical for the apatite composition can result in marked decreases in the apatite phase and in turn in the OH ion content as compared to the stoichiometric fully hydroxylated apatite. For example, an apatite preparation with a net M:P molar ratio of 1.650, only 1% lower than the theoretical molar ratio 1.667, corresponding to a composite composition on ignition of $3M_{10}(PO_4)_6(OH)_2 + M_3(PO_4)_2$ would be about 10% lower in OH ion content than the stoichiometric composition and would contain about 10 wt % $M_3(PO_4)_2$. Only apatite was detected in the final preparations used for the intensity comparisons and a second phase of $M_3(PO_4)_2$, if present, was less than about 5 wt %. The lack of spectroscopic evidence for $M_3(PO_4)_2$ and other phases $M_2P_2O_7$, $M_4(PO_4)_2O$, MCO_3, MO (as hydroxides), or MO_2 indicates that the apatite preparations were essentially stoichiometric and that the reactions went to completion. In addition, the chemical analyses for phosphorus, which are close to the theoretical values, further indicate that the preparations were essentially stoichiometric.

The actual crystal size of these preparations was not determined. Petrographic examination of the ground preparations indicated the major phase of the conglomerated materials to be composed of birefringent particles greater than 1 μ in size, although mosaic-type composition of the small particles was not excluded. However, X-ray diffraction line profiles, approximately the same for all three apatites, indicated well-crystallized materials and *a*- and *c*-axis crystal dimensions not less than about 1000 Å. Because of the low surface-to-volume ratio of apatite crystals with *a*- and *c*-axis dimensions 1000 Å and greater, the degree of spectral alteration caused by the fractions of surface and internal unit cell experiencing different environments is expected to be small, about 5% if a surface environment one unit cell thick is considered. All of the apatites were well crystallized as indicated by the sharpness of the phosphate absorption bands. Hence, the OH band intensity variations do not appear to arise from differences in crystal size or crystallinity.

Because of the markedly lower OH band intensities of Ba(OH)A, samples of the Ba(OH)A starting material, prepared at 900-1100° in 1.5 atm H_2O vapor, were further heated in air and in sealed Vycor glass tubes containing H_2O. Spectra of the Ba(OH)A treated at 300° (240 hr) and 600° (140 hr) in air and at 5 and 25 atm H_2O pressure and at 900° (66 hr) in air all showed Ba(OH)A and no major differences in the OH band intensities. Spectra of the Ba(OH)A ignited at 900° (24 hr) at 5 and 25 atm H_2O pressure showed a second phase of $Ba_3(PO_4)_2$ and the probable third phase, $Ba(OH)_2$, was not unequivocally identified, but extremely weak absorption was observed at about 3575 cm^{-1} which is close to the $Ba(OH)_2 \cdot H_2O$ OH stretching doublet (3580 and 3568 cm^{-1}) centered at 3574 cm^{-1}.[41] There were very slight spectral indications of $Ba_3(PO_4)_2$ formation in the Ba(OH)A samples ignited at 300 and 600° at 5 and 25 atm H_2O pressure. The Ba(OH)A ignited in air at 1260° (25 hr) also showed a second phase of $Ba_3(PO_4)_2$ and an increased CO_3 content.

The OH band intensities of a precipitated sample of Ba(OH)A prepared using the concentrations and conditions described by Artur[42] and summarized by Mooney and Aia[43] were even weaker than those of the hydrothermally prepared samples.

No definite apatite OH bands other than the Sr(OH)A and Ba(OH)A bands at 3592 and 3606 cm^{-1}, respectively, were detected in the 4000-2000-cm^{-1} region. The broad absorption in the 3500-cm^{-1} regions of Sr(OH)A and Ba(OH)A[4] is not attributed to apatite structural OH ions bonded differently than the apatite OH ions absorbing at 3592 and 3606 cm^{-1}, but rather to adsorbed water because no absorption occurs in the corresponding regions below the OD stretching frequencies.

In summary, the OH band intensity differences in these apatites do not appear to arise from OH deficiency, substitution of other ions (F^-, Cl^-, O^{2-}, $CO_3{}^{2-}$) for the OH ion, stoichiometry, crystallinity, particle size, index of refraction of the sample pellet, crystal orientation, or multiple OH bands arising from different environments about the OH ions. These factors and others will require consideration in

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spectral evaluation of the OH ion in biological apatites.

It appears reasonable to assume that the OH band intensity variations arise from differences in bonding imposed by the crystal fields on the OH ions in these apatites. The intensity of each OH band is dependent upon the square of the change in dipole moment which, in turn, depends upon the change in the electrical character of the atoms as they vibrate according to the coordinates which describe the vibration. It is apparent from the decreases in the OH band intensities that the dipole moment changes during the OH vibrations become progressively weaker in the Ca-, Sr-, Ba(OH)A sequence.

The intensities of OH bands of selected organic alcohols (R-OH) decrease as the electron-withdrawing power of the R group decreases.[44] The electronegativity of Ba (0.9) is less than those of Sr (1.0) and Ca (1.0), and the lower electron-withdrawing power at the center of the trigonal Ba plane may contribute to the lower OH band intensity. As previously discussed, the relative frequency shifts of the OH modes in the Ba-, Sr-, Ca(OH)A sequence as a function of assumed decreasing OH to PO_4 intermolecular distances are suggestive of a progressively stronger hydrogen-bond interaction. The progressively enhanced OH band intensities in this sequence are also consistent with a progressively stronger hydrogen bond interaction; however, there are essentially no increases in the band widths which are concomitant with stronger hydrogen bonding. The polarizing powers (e/r^2, where e is the ionic valence and r the ionic radius) of Ca, Sr, and Ba are 2.04, 1.59, and 1.11, respectively. A decrease in polarization of the OH ion decreases the tendency of the OH ion to form hydrogen bonds. The progressive decrease in cation polarizing power in the Ca-Sr-Ba sequence correlates with and may contribute to the possible OH- - -OPO_3 interaction and in turn to the decreases in OH band intensities.

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Registry No. $Ca_{10}(PO_4)_6O$, 12265-54-2; $Ba_{10}(PO_4)_6O$, 12397-85-2; $Sr_{10}(PO_4)_6O$, 12266-36-3; H_2O, 7732-18-5; $H_2{}^{18}O$, 14314-42-2; D_2O, 7789-20-0; Ca(OH)A, 1306-06-5; Ba(OH)A, 12356-34-2; Sr(OH)A, 12266-00-1; ^{44}Ca, 14255-03-9; ^{48}Ca, 13981-76-5; $Ca_5(OH)(PO_4)_3$, 12167-74-7; $Ba_5(OH)(PO_4)_3$, 12377-63-8; $Sr_5(OH)(PO_4)_3$, 12195-53-8.

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Octahedral Hexafluoro Complexes of the Tetravalent Actinides[1]

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Salts and solutions of the octahedral $UF_6{}^{2-}$, $NpF_6{}^{2-}$, and $PuF_6{}^{2-}$ ions were prepared. These represent a lower coordination number than previously known for tetravalent actinides in fluoro complexes. Absorption spectra of these hexafluoro complexes in the region of internal f-electron transitions are presented and are the weakest known for U(IV), Np(IV), and Pu(IV).

Introduction

Until relatively recently many scientists believed that six was a common coordination number, N, for trivalent and tetravalent actinides and lanthanides. The excellent work of Satten, *et al.*,[3-5] on the detailed interpretation of the internal f-electron transition spectra of salts of the octahedral $UCl_6{}^{2-}$ ion at low temperature showed that, as predicted by theory for an ion having O_h symmetry, the electronic transitions are missing and only relatively weak vibronic transitions are present. This and the finding that the overall molar absorptivities of the $UCl_6{}^{2-}$, $NpCl_6{}^{2-}$, and $PuCl_6{}^{2-}$ ions were markedly lower[6] than those then known for other U(IV), Np(IV), and Pu(IV) solutions along with slowly increasing X-ray evidence of the common existence of high coordination numbers for lanthanides and actinides raised suspicion that $N = 6$ might be uncommon for tetravalent and trivalent actinides and lanthanides. The preparation of hexabromo and hexaiodo complexes of the tetravalent actinides and the finding of low molar absorptivities for these complexes confirmed this and led to the conclusion that the tetravalent actinides normally prefer $N = 8$ or 9 with F^- or oxygen-containing ligands.[7] Later preparation of trivalent lanthanide[8] and actinide[9] hexahalide complexes and comparison of their absorption spectra to those of various other lanthanide and actinide species resulted in the conclusion that $N = 6$ is very rare indeed for the trivalent actinides and lanthanides.

In the last few years, the amount of X-ray structural analysis has increased rapidly, and it is now known that $N =$ 8, 9, 10, or 12 is much more common for trivalent and tetravalent actinides than is $N = 6$, and even with the smaller hexavalent actinides, $N > 6$ is common. In particular the fluorides have been much studied, and although $N = 6$ in the neutral hexavalent MF_6, several addition compounds with alkali and other fluorides are known[10] indicating a strong

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